OBSERVATION OF ATMOSPHERIC TRACE CONSTITUENTS BY FTIR (EXTENDED ABSTRACT)

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1. Introduction

Absorption bands of $CFCl_3$, CF_2Cl_2, HNO_3, N_2O and CH_4 were observed in infrared sunset solar spectra in the 700–6000 cm^{-1} region at mid-latitudes (34°–36°N). Two halocarbons ($CFCl_3$ and CF_2Cl_2) and N_2O are thought to be major sources of the stratospheric ClO_x and NO_x, respectively (MOLINA and ROWLAND, 1974; OGAWA, 1976; CRUTZEN, 1971; MCELROY and MCCONNELL, 1971). Also CH_4 is an important source of CO and H_2O, and produces various forms of hydrocarbons and HO_x in the stratosphere (CRUTZEN, 1973). On the other hand, HNO_3 is important as a sink for stratospheric NO_x (CRUTZEN, 1971; JOHNSTON, 1971).

In order to assess the influence of these components, especially CF_2Cl_2 and $CFCl_3$, on the natural ozone balance, the atmospheric concentrations and distributions of them must be known over the whole globe including the Antarctic zone. We are preparing to monitor their behavior at Syowa Station, Antarctica.

2. Instrumentation and Observations

Concentrations of $CFCl_3$, CF_2Cl_2, HNO_3, N_2O and CH_4 are so small that we made direct sun measurements during sunset or sunrise to take advantage of the long path-length. Moreover to avoid the effects of absorption by water vapor and carbon dioxide, observations were made on an aircraft at the altitude of 7–8 km.

The sun-follower allowed sunlight to enter a Fourier transform infrared spectrometer (FTIR), which has a spectral resolution of 1.0 cm^{-1}. Two detectors of InSb (for 2–5.5 μm) and HgCdTe (5.5–14.5 μm), which were cooled to liquid nitrogen temperature (77 K), were on the aircraft, and one or the other of them was used. When the instrument was mounted in the aircraft the interferograms in digital form were stored on magnetic tape. Interferograms were transformed to spectra by mini-computer in the laboratory.

More than ten series of operations have been carried out since October 1979. However, only the observations on January 7, 8 and 9, 1981 satisfied the condition that the solar elevation was low enough and the absorption spectra were recognizable.

3. Results and Discussion

We show an example of a solar spectrum in Fig. 1. Absorption bands of $CFCl_3$ (centered at 847 cm^{-1}), HNO_3 (897 cm^{-1}) and CF_2Cl_2 (923 cm^{-1}) are confirmed in the 770–970 cm^{-1} region, where absorptions by H_2O, CO_2 and O_3 are zero or small (MAKINO *et al.*, 1982).

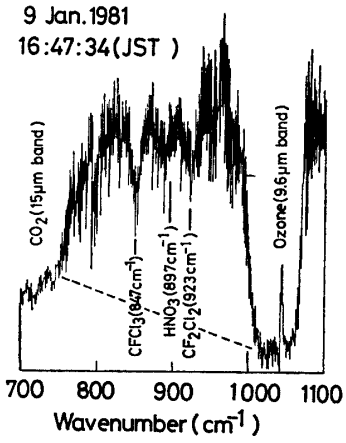

Fig. 1. A part of the infrared solar spectrum obtained with the HgCdTe detector at 16:47:34 JST, on January 9, 1981, from an altitude of 7.8 km over the Kanto District, when the solar zenith angle was 90.9.

The transmittances of band centers were corrected using the synthetic spectra. According to the statistical spectral band model (GOLDMAN *et al.*, 1971, 1976a, b), these absorption bands were analyzed. The mean mixing ratios and the standard deviations were 280±16 pptv for CF_2Cl_2 and 183±16 pptv for $CFCl_3$, assuming unifrom mixing along the optical path. These values agree with the values of 294±10 pptv for CF_2Cl_2 and 184±13 pptv for $CFCl_3$ obtained from grab sampling in the upper troposphere and lower stratosphere over Japan (HIROTA *et al.*, 1982). Similar values for $CFCl_3$ in the upper troposphere at mid-latitudes of northern hemisphere have been obtained by some investigators (GOLDAN *et al.*,

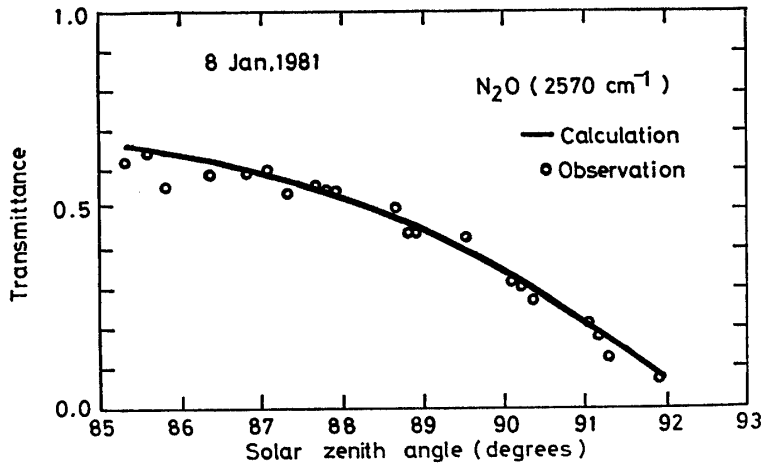

Fig. 2. Transmittances at 2570 cm^{-1} of the N_2O band observed and calculated, with the same resolution of 1 cm^{-1}. The accuracy of each observation is ±0.05, however, this is not indicated in the figure.

1980; LEIFER *et al.*, 1981), but smaller ones have been obtained by others (FABIAN *et al.*, 1981). For CF_2Cl_2, GOLDAN *et al.* (1980) and FABIAN *et al.* (1981) obtained similar values to ours but LEIFER *et al.* (1981) larger one.

The vertical profiles of HNO_3 mixing ratio observed by MURCRAY *et al.* (1973) show the peak layer between the altitudes of 18–28 km. Therefore, assuming the uniform mixing between the altitudes of 18 km and 28 km the mixing ratio of 9.06 ± 1.83 pptv for HNO_3 was derived. This value is larger than those obtained by MURCRAY *et al.* (1973) and LAZRUS *et al.* (1972), but agrees with a value deduced from a one dimensional numerical model (MURAMATSU *et al.*, 1982).

In an other part of the infrared solar spectra obtained with the InSb detector, absorption bands of N_2O (2570 cm^{-1}) and CH_4 (6004 cm^{-1}) have been clearly confirmed. These spectra are in good agreement with the synthetic spectra calculated for the model atmosphere, in which the mixing ratios are 0.310 ppmv for N_2O (see Fig. 2) and 1.5 ppmv for CH_4 in the upper troposphere.

In the Antarctic zone, a few observations of these trace gases have been reported (RASMUSSEN, 1978; HOFMANN *et al.*, 1978, 1979; RASMUSSEN *et al.*, 1981). In addition to their roles in ozone layer chemistry, it is also very interesting from the view point of atmospheric global circulation to measure these trace gases. $CFCl_3$ and CF_2Cl_2 are good tracers of atmospheric motion because they have only anthropogenic origin, located mainly in the northern hemisphere, and have a long life time in the troposphere.

We are now preparing to monitor these trace gases at Syowa Station, Antarctica, as a part of the Special Project for the Antarctic Middle Atmosphere. Our preliminary results, described above, show the standard deviations of 6, 9 and 20% (numbers of samples, are 14, 10 and 15) for CF_2Cl_2, $CFCl_3$ and HNO_3, respectively. The typical accuracy of each measurement was $\pm 20 \sim 30\%$ for CF_2Cl_2 and reached as high as $\pm 60\%$ for HNO_3. In the plan, the following improvements of experimental conditions are expected:

(1) measurements from a ground based station instead of on board an aircraft,
(2) larger effective cross-sectional area of sun-follower,
(3) high resolution of about 0.12 cm^{-1} and use of the appropriate band-pass filter.

Because of the dry atmosphere, it is advantageous to take observations of solar infrared spectra, that is to say, absorption bands of trace gases, in Antarctica.

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